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LUMINESCENT MATERIALS AND THEIR APPLICATION TO LIGHT SOURCES

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(Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley, England.)

(Paper read on Tuesday, April 12th, 1938.)

Introduction.

Not so long ago the majority of luminescent effects, although providing some of the most fascinating of lecture experiments, had little practical application. In the past few years, however, the luminescence of gases and vapours, under the action of the electric discharge, has been utilised on a large scale. In fact, as a result of intensive development work, many new varieties of light source, depending on this once abstract phenomenon, have recently emerged.

Discharge lamps convert electrical energy into radiation characteristic of the gas or vapour employed. But, since the choice of medium is for many reasons very limited, the colour of the emitted light is more or less restricted to a few well-recognised types. In fact, it is becoming not uncommon to hear the terms "Mercury Light," "Sodium Light," and "Neon Light." Although each has its use, the field of discharge lamp lighting would be materially extended if the colour of the light could be more completely controlled. Moreover, the luminous efficiency of the lamps, though high, is far below that theoretically possible, since, in addition to the visible light, they emit a considerable amount of invisible radiation. If means could be found to convert an appreciable part of this into useful light, the efficiency would be raised considerably.

The improvement in colour control and efficiency by the utilisation of the ultra-violet portion of the invisible radiation, constitutes what may be called a second stage in the development of discharge lamps. It is of no little interest that, whereas in the first stage of their development the lamps depended on the utilisation of the electro-luminescence of gases and vapours, in this second stage they depend on the related phenomenon of photo-luminescence of solids. It is with the last-mentioned and cognate effects that this paper will be chiefly concerned.

Definitions.

Luminescence is generally defined as any emission of light other than ordinary temperature radiation. The term thus includes phenomena as widely different as phosphorescence, whether produced by light or any other agency, and the emission of light by gases under the action of the electric discharge. Particular types of luminescence are distinguished by the use of various prefixes. Thus, for example. when light is the exciting agency, the phenomenon is designated photo-luminescence, while the term chemi-luminescence is used to include cases in which an emission of light accompanies chemical reactions; the closely related phenomenon of the emission of light by living organisms is called bio-luminescence.

Photo-luminescence which is exhibited only so long as the stimulating radiation falls on the substance is spoken of as *fluorescence*, while the word *phosphorescence* is used if the luminescence persists for an appreciable time after irradiation is stopped. The distinction is, however, not an exact one, since, strictly speaking, the emission never ceases instantaneously when the exciting light is cut off.

The name fluorescence was applied to the transient phenomena by Stokes, who derived the word from Fluor Spar, a natural mineral which often shows the effect to a remarkable degree. Phosphorescence, on the other hand, is derived from the well-known glow exhibited by the element phosphorus, while undergoing oxidation; the term also has a wider meaning than that defined above, and is often used to describe any persistent luminescence, irrespective of its cause.

Historical.

Bio-luminescence must have been noticed even in prehistoric times. The ancients would almost certainly have wondered at glow-worms, fireflies, and the even more mysterious phosphorescence of the sea. They would surely also have observed the brilliant, bluish-white glow emitted by the minute fungus which, under suitable conditions, infests decaying wood.

The earliest known application of luminescent materials seems to have been made by the Japanese. In the records of the Sung Dynasty, about 980 A.D., there occurs the charming story of a magic picture, in which an ox appeared every evening at dusk, though it left to graze during the daytime. The Chinese Emperor, Tai Tsung, sent for the picture and showed it to his court, whereupon a priest resolved the mystery.(1). He explained that the Japanese were able to prepare a luminous material by calcining oyster shells, and that by mixing this with their pigments they could introduce into paintings objects which, though invisible by day, appeared at night owing to their luminescence.

The art of preparing luminous substances then seems to have been lost until 1602, or possibly 1630, when Vincentius Casciarolus, a shoemaker of Bologna, who dabbled in alchemy, accidentally discovered another method. He was experimenting with a mineral, later known as Heavy Spar, which he had obtained in the neighbourhood of Monte Paterno, not far from the town. He was hoping to extract silver and therefore tried mixing the mineral with a combustible substance and heating the mixture to redness for some time. No silver resulted, but instead he found that his preparation had the remarkable property of glowing in the dark for an appreciable time after it had been exposed to light. This luminescent substance became famous as the Bologna Stone and was studied by many philosophers of the period. It gave an orange-red phosphorescence

which was visible in the dark, sometimes for nearly half an hour, after only a few seconds' exposure to sunlight. For a long time Heavy Spar was believed to be a variety of Gypsum, and it was not until much later that it was recognised as a distinct mineral species now known as Barytes. Chemically this is barium sulphate, which the heat treatment would have reduced to barium sulphide.

In 1768, about one hundred and fifty years later, the Englishman Canton ([2]) prepared a luminescent calcium sulphide by heating ground oyster shells with flowers of sulphur; the heating was done in a crucible embedded in a coal fire. The resulting compound became known as Canton Phosphorus, and gave a glow which varied from yellow-green to bluish-green in different preparations.

It may be of interest to note here that among the many investigators who studied these peculiar substances was the German poet Goethe, who was also a natural philosopher of some repute. While staying at Bologna, in 1786, he visited Monte Paterno and collected specimens of the local Heavy Spar. Not only did he send samples of the luminous "cakes," prepared from this, to many of his friends, but he himself seriously investigated their properties. One of his most striking experiments consisted in exposing the material to light of different colours, and this led him to the discovery that the phosphorescence could be excited only by blue light, and not by red or yellow. Moreover, he was the first to observe the extinction effect of red light, which will be discussed below. His great enthusiasm for these studies seems to have coloured his poetical work as well; the second part of Faust, in particular, shows a great pre-occupation with luminous effects of all kinds. Moreover, an early draft of the first part contained an actual mention of the Bologna Stone, but this was deleted in the final version ([3]).

A third "classic" luminous compound, or phosphor, was discovered in 1867 by the Frenchman Sidot. This is a zinc sulphide, and has long been spoken of as Sidot's Blende; it phosphoresced with a brilliant green light. The original method of preparation was to sublime specimens of the mineral Sphalerite, or Zinc Blende, which, as is now known, happened to contain copper as an impurity.

Towards the end of the last century an improved preparation of calcium sulphide, obtained by heating lime and sulphur with a trace of bismuth, appeared on the market under the name of Balmain's Paint. This compound gives a bright blue-violet phosphorescence which continues visible in the dark for an hour or more after exposure to light. In the early days the results of attempts to produce the luminous compounds were most uncertain. Preparations varied so greatly in their degree of phosphorescence that materials produced at different times, by apparently identical methods, might either be brilliantly phosphorescent or almost inactive; the colour of the emitted light was also very variable.

Lecoq de Boisbaudron ([4]) was the first to conclude, in 1886, that the presence of an impurity was necessary to produce the desired effect, and he suggested that phosphors were solid solutions of the impurity in the crystals of the main substance. The variability of the early attempts was thus attributable to the fact that the important impurity occurred fortuitously in the mineral substances used.

These views were confirmed, at about the same time, by Verneuil ([5]), who also found that more regular and better results were obtained if a flux, such as sodium chloride or carbonate, was introduced into the mixture before calcining.

It was found that the amount of the impurity, or activator, needed to be accurately controlled: if too much or too little were present, poor luminosity would result. Furthermore, the activator, generally a metal of high or moderately high atomic weight, had to be chosen to suit the particular compound. Thus bismuth was found to be most effective for calcium sulphide, while copper was best for zinc sulphide.

Throughout the last century, the interest in luminescent effects continued to grow and more fundamental investigations of the subject began to be made, in particular by Becquerel([6]) and Stokes([7]). In 1852, the latter enunciated the well-known law which still bears his name. This states that the wavelength of the emitted light is always greater than that of the exciting radiation. The law is generally borne out in practice, but many exceptions have been observed, notably in the behaviour of vapours and of solutions of fluorescent organic compounds. Less marked violations of the law have been found with solid phosphors. For example, using the 4358 A. mercury line as the exciting radiation, it is possible, with a calcium sulphide-bismuth phosphor, to observe phosphorescence of wavelengths extending slightly to the violet side of the line.

The fact is that the quantum energy of the emitted light cannot be greater than that of the exciting light, unless additional energy is introduced. Accordingly, the occurrence of photo-luminescence of a wavelength shorter than that of the exciting light is simply an indication that the electrons responsible for the emission have acquired energy in excess of that derived directly from the exciting radiation. Frequently the extra energy is supplied by molecular thermal agitation, but it may arise in other rather more obscure ways. The excess energy which can be acquired is generally quite small, in comparison with the quantum energy of the exciting light, so that departures from the original simple formulation of the law are not large. Stokes's law thus remains a useful rule in spite of the exceptions.

Before dealing in detail with more recent work on photo-luminescent solids and with their properties, it will be convenient to review briefly certain other important classes of luminescent effects.

Chemi-Luminescence.

The classic example of chemi-luminescence is that exhibited during the oxidation of moist phosphorus. This element was discovered in the latter part of the seventeenth century by Hennig Brand, of Hamburg, who was a zealous alchemist. When his experiments revealed the white, waxy, light-giving element, Brand called it cold fire, "kaltes Feuer," or, affectionately, "mein Feuer." The great mathematician Leibnitz was personally acquainted with Brand,

and, becoming actively interested in the remarkable material, wrote a history of its discovery. He often exhibited small phials, containing specimens of the new element, which shone like glow-worms in the dark, and he suggested that sufficiently large pieces of the substance might give enough light to illuminate an entire room. Leibnitz was told, however, that this would be impracticable, because the process of preparation was too difficult. This objection does not, of course, apply nowadays, but the proposition still remains out of the question for obvious reasons. It is of interest, however, to record the luminous efficiency of the reaction, for comparison with other light sources. The measurement has been made by Adams ([8]), who photometered the cone of luminosity produced when a stream of nitrogen, saturated with phosphorus vapour, escapes into the air. The power input was determined from the measured flow of the nitrogen and the heat of oxidation and vapour pressure of phosphorus. The ratio of the light flux to the power input came out to be of the order of one lumen per kilowatt. It is seldom one finds a light source so thoroughly inefficient!

A large number of other reactions give rise to chemi-luminescent effects, and some of these are far more efficient. If pyrogallic acid, such as is used as a developer in photography, is treated with hydrogen peroxide, the oxidation of the pyrogallol is accompanied by an emission of light. The addition of potato juice improves the effect, since it contains an enzyme which acts as a catalyst and thus assists the transfer of oxygen from the peroxide to the pyrogallol. A particularly effective reaction is the oxidation of o-aminophthalic cyclic hydrazide([9]). The luminescence is well shown when sodium hypochlorite is mixed with a weakly alkaline solution of this compound. The intensity of the light is materially improved by the presence of hydrogen peroxide and catalysts such as potato juice. With a concentrated solution the glow can be seen in daylight, while to the dark adapted eye, a faint glow is said to be perceptible even at dilutions of one part in a hundred million.

Bio-Luminescence.

Many living things emit light, either continuously or in flashes. The more lowly luminous organisms, for example certain bacteria and fungi, generally give out light all the time, while the emission from the more highly organised creatures, such as fireflies and luminous fishes, is often intermittent. Several varieties of luminescent bacteria are known, the most commonly observed being those which grow on decaying fish. The phosphorescence of damp, decaying wood, on the other hand, is due to a minute mycelium, or fungus, called *Agaricus Melleus;* under suitable conditions its luminosity can be surprisingly high. Displays of phosphorescence of the sea are due to the presence of innumerable small organisms, generally protozoa. These emit light when stimulated and, for this reason, the effect is usually only seen when the water is violently agitated.

Bio-luminescence is always dependent on the presence of oxygen. As early as 1667 Robert Boyle showed that a piece of phosphorescent wood, which he placed in the receiver of his air pump, stopped glowing when the air was removed. The glow soon appeared again, however, when air was readmitted. Another interesting early discovery is that bio-luminescent material can be preserved for some time if it is rapidly dried; later, when moisture is added, the light will reappear. Later work has shown that the dried material retains its properties for years if kept in sealed tubes with an atmosphere of hydrogen.

Coming to more recent times, an important discovery was made by Dubois, who found that, apart from water and oxygen, there are two special types of chemical compound necessary for luminescence; these substances, called Luciferin and Luciferase, are synthesised by luminescent organisms.

Subsequently a great deal of work on the nature and properties of these substances has been done, particularly by Harvey.([10]) Luciferase has been shown to be an enzyme which catalyses the oxidation of luciferin; in fact, no action takes place unless it is present. The two compounds can be separated in the laboratory and the luminosity can then be produced at will by mixing them together. Bio-luminescence has thus proved to be a particular class of chemi-luminescence.

Another important discovery was made by Harvey, who showed that the oxidation process was a reversible one. Thus, in the presence of oxygen and the necessary enzyme, luciferin emits light during its oxidation; then, by the action of hydrogen and colloidal palladium, for example, the resulting waste product, oxy-luciferin, can be reduced to luciferin once more and the process repeated. Indeed, both reactions can take place simultaneously in one vessel, so that a continuous emission of light can be obtained for quite a long time, provided that the supply of both oxygen and hydrogen is maintained. However, owing to practical difficulties, it is not possible to obtain nearly such a high brightness in this way as in the simple case of the direct oxidation of luciferin.

Compared with more usual light sources the brightness of all bio-luminiscent effects is very low. Ives ([11]) has measured the intrinsic brilliancy of the glow worm and found it to be 0.005 candles per sq. cm., so that a luminous area of two square metres would be necessary to give a hundred candle-power. Coblentz ([12]) found a higher brightness in the case of the firefly and measured a maximum value of 0.02 candles per sq. cm.

Many measurements have also been made of the luminous efficiency of these sources. Certain fireflies, whose light consists of wavelengths lying in a narrow band, closely resembling the visibility curve of the human eye, appeared to have a luminous efficiency vastly higher than that of any other known source, since no sign of any ultra-violet or infra-red radiation could be observed. Thus the efficiency, defined as the ratio of the visible to the total amount of energy radiated, was nearly unity. Taking into account the wavelength energy distribution, this would be equivalent to about 200 lumens per watt of the observed radiated energy. Later work has, however, shown that the *overall* efficiency is actually not nearly so high, because heat is evolved during the

oxidation of luciferin. When this is taken into account the efficiency comes out to be between 1 and 10 lumens per watt. The heat of the reaction is distributed by conduction in the animal and it entirely escaped detection in the earlier experiments.

It has often been suggested that chemi- and bioluminscent effects might be used for illuminating purposes. For example, it has been conjectured that rooms might be lighted by means of an extensive system of glass tubes, through which the necessary liquids could be circulated. It has even been proposed to make lamps of glass bulbs containing cultures of luminescent bacteria; such lamps could, presumably, be turned on and off by regulating the oxygen supply. As may be imagined, all such schemes have, up to the present time, proved quite impracticable, but one would hesitate to say that, in the future, chemi-luminescent effects will never have applications as light sources, at least for specialised purposes.

Flame Luminescence of Solids.

In the case of the pure temperature radiation from heated solids, the radiated energy corresponding to any given wavelength cannot be greater than that of a black body at the same temperature. Radiation whose intensity is in excess of this is, however, observed when certain substances are heated in particular zones of hydrogen or similar flames; the active zone is generally that part lying between the oxidising and reducing regions. The excess radiation, which is due to luminescence, occurs only within definite ranges of temperature and within certain wavelength limits ([13]). It is clear that the effect is due to excitation by the flame, since the luminescence does not occur when the substances are heated to the same temperature in vacuo or in air without the flame. Often luminescence is observed in two wavelength bands, each having its characteristic temperature range. For example, zinc oxide has been found to give an excess of red radiation between 568° C. and 704° C., and an excess of green between 704° C. and 948° C. Some photo-luminescent compounds are also excited when in contact with flames. Thus activated zinc silicate, spread on a sheet of metal, glows with a bright green colour when a gas flame is lightly brushed over it.

Similar effects are observed with the oxyhydrogen flame([14]) and, when slightly heated by it, many oxides emit a blue luminescence, superimposed on the ordinary temperature radiation. At higher temperatures the luminescence becomes inappreciable and the radiation is then purely thermal. Luminescence is said to occur in the ordinary lime light, particularly when the calcium oxide block is fresh. It has been suggested([15]) that the fall in brightness, which is observed over a period of half an hour, is due to fatigue of this luminescence; the loss of intensity has been shown to be greatest at the blue end of the spectrum.

Photo-luminescence of Organic Substances.

Photo-luminescence of organic compounds is by no means a rare phenomenon; in fact, nearly all fluoresce to some extent, under suitable conditions. Paper and the human teeth, for example, fluoresce with a whitish light, while numerous other organic compounds give brilliantly coloured effects. The after-glow of the luminescence is generally very short, and it is only in exceptional cases that it is of sufficient duration to merit the name phosphorescence. Organic compounds may exhibit fluorescence when in the form of liquids or solids, and sometimes when in the vapour state. In the former cases, the spectrum of the emitted light consists of one or more bands, typical examples of which are shown in Fig. 1. Fluorescent vapours also give band spectra, but the bands can be resolved into multitudes of fine lines.

Fluorescent organic materials may be divided into two important classes. Those of the first class, although fluorescent in the pure state, generally lose

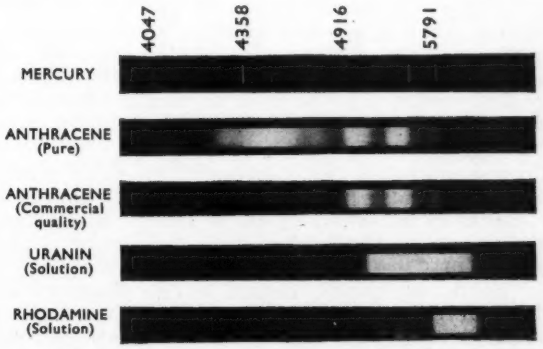

Fig. 1. Spectra of luminescent organic compounds.

their fluorescence when in solution. As examples the crystalline solids anthracene, fluorene and phenanthrene may be mentioned. Commercial anthracene often gives a bright green fluorescence, but when the material is highly purified, the fluorescent colour is always bright blue. A solution of this material in benzene is non-fluorescent, but fluorescence occurs as the solvent evaporates and the compound crystallises out of solution.

In contrast to this behaviour, compounds of the second class show little or no fluorescence when in the solid state, but give brilliant fluorescence when in liquid or solid solution. Examples of this type are quinine and a large number of organic dyestuffs such as fluorescein, rhodamin and eosin. Dispersion of the material in a finely divided state is not sufficient; it is necessary that the individual molecules of the substance be in intimate association with molecules of the solvent or medium, rather than with one another. In view of this, it is not surprising that the particular solvent used influences not only the intensity of the fluorescence, but also to some extent the spectrum of the light emitted. The emission band generally moves slightly towards the red end of the spectrum as the dielectric constant of the solvent increases.

The concentration of the material in solution is also important. Thus neither solid uranin, the sodium salt of fluorescein, nor a saturated solution of it is fluorescent; indeed, a dilution of some twenty

times is necessary before traces of light emission begin to be seen. The intensity of the fluorescence increases with further dilution, passes through a maximum, and then steadily diminishes. In the case of this material, the most minute trace still gives a perceptible effect; in fact, using sensitive methods, the fluorescence has been definitely recognised at a dilution of 10^{-14} gram per cc. in water.

The duration of the luminescence of liquid solutions is generally less than a millionth of a second, but if the viscosity of the solution is increased, by the addition of gelatin, for example, the duration of the after-glow increases, although it still remains short. If, however, the gelatin is dried to form a solid film, the after-glow may increase so much as to be readily noticeable. This effect is well shown by aesculin, a substance which occurs in the horse-chestnut tree. particularly in its sticky buds and bark. This material, when in aqueous solution, gives a beautiful blue fluorescence, with no perceptible after-glow, but when it is present in a dried gelatin film, a green phosphorescence may be seen to persist for several seconds. Freezing a solution of aesculin also increases the after-glow time.

Corresponding to the fluorescent emission bands, the materials also have absorption bands, and it is the radiation absorbed in these latter wavelength regions that is transformed into fluorescent light; radiation of wavelengths falling outside the absorption band, or bands, cannot excite fluorescence. Furthermore, the modern forms of Stokes's law states that excitation occurs only within an absorption band which, though it may overlap the fluorescence band, always has its " centre of gravity " at a shorter wavelength. Of course, the presence of an absorption band does not necessarily mean that the material will be fluorescent.

In addition to Stoke's law three further important rules relating to fluorescence are as follows:—

(1) The shape and position of the fluorescence band remains the same, independently of the wavelength of the exciting light.

(2) As the wavelength of the exciting light is varied, the intensity of the fluorescent light is approximately proportional to the energy absorbed in the corresponding absorption band.

(3) For a constant wavelength of exciting light, the intensity of the fluorescence is proportional, over a wide range, to the energy of the light absorbed.

One other important phenomenon, namely, the fading effect, remains to be discussed. Various fluorescent organic solutions, both solid and liquid, are found to lose their fluorescence more or less rapidly on exposure to strong light; this effect has been studied in some detail by Perrin ([16]) and Wood ([17]). With intense radiation, thin films of anthracene in xylol, for example, become inactive after only a few seconds' exposure. In the same way, solutions of fluorescent dyes, such as eosin and rhodamin, become bleached in quite a short time if the light is sufficiently strong. The destruction of the fluorescent material sometimes involves several successive change; thus phenosafranine, which to start with gives a yellow fluorescence, is first converted to a compound giving a green colour, and this, after a short additional exposure, changes finally into a quite inactive substance. In simple cases, the absorption and fluorescence bands remain in their usual positions during the exposure, but their intensity gradually decreases, until they fade out altogether. In the more complex cases the original bands fade out as before, but new ones appear, only to fade out in their turn. The effect is clearly due to chemical changes brought about by the light, and it is therefore not surprising that the rate of fading depends upon the solvent used. Of course, the light causing fading must be of wavelengths falling within the region of absorption, but it would appear that, in some cases at least, the particular wavelengths which are most active in producing the chemical changes are not necessarily those which are most active in producing luminescence.

Photoluminescence of Pure Inorganic Compounds.

Inorganic luminescent compounds can also be divided into two classes, namely, those which require the presence of an activator and those which do not. With very few exceptions the latter exhibit only fluorescence, while the former frequently show phosphorescent effects as well.

The chief compounds which fluoresce in the pure state are the platinocyanides and the uranyl salts, together with certain tungstates and molybdates. Although there is no doubt whatever that the former two compounds fluoresce without activators, it is not absolutely certain that no activator is necessary in the latter cases, although it may not be of the usual type. Activators are, however, almost always present, either by accident or design, in tungstate and molybdate preparations; some of the effects they produce will be mentioned in the next section.

The best known platinocyanide is the barium salt $BaPt(CN)_4.4H_2O$ which gives a bright yellow-green fluorescence under ultra-violet light. This is the compound which was formerly used almost exclusively for X-Ray screens, until it was superseded by special sulphide preparations mentioned below. Other compounds of this class give a wide variety of colours, although none is so bright as the barium salt. Thus lithium platinocyanide gives an orange colour, while the potassium, rubidium, and calcium salts give blue.

All the platinocyanides fluoresce only in the crystalline state, and their brightness varies with the amount of water of crystallisation that is present, so that in each case there is one particular hydrate that gives the best effect. No luminescence occurs when the compounds are in solution and very little when they are anhydrous.

The uranyl (UO_2) salts, on the other hand, fluoresce in the pure crystalline state and also when in liquid or solid solution, but uranium dioxide itself is non-fluorescent. When, however, the latter is dissolved in glass it imparts to it a strong green fluorescence; a further addition of cadmium oxide produces the well-known " Canary " glass. More recently both

varieties have been employed in the form of tubing for low pressure, high tension mercury signs.

Barium platinocyanide and the uranyl salts can be excited by a wide range of wavelengths, extending from the violet to the far ultra-violet region of the spectrum; the tungstates and molybdates, on the other hand, respond, in general, only to the shorter wavelengths. Among the latter class, the chief compounds of interest are calcium tungstate and magnesium tungstate; the former gives a fluorescent band at the blue end of the spectrum, while the latter emits light in a band which extends all the way from the blue to the orange region. The molybdates give less brilliant effects.

Photoluminescence of "Activated" Inorganic Solids.

The compounds in this class, which includes all the "classical" phosphors, are characterised by the fact that their luminescence depends on the presence of small quantities of "activators" such as copper, bismuth, or manganese. Solid solution of the activator in the "matrix" is essential. Although it is possible, in some cases, to achieve this state by fusing together appropriate salts of matrix and activator at comparatively low temperatures, the resultant materials have, in general, little practical use; they often deteriorate rapidly or evolve gas when used in a discharge tube. The more stable materials, such as sulphides and silicates, cannot be prepared by such simple means; high temperature treatment, under carefully controlled conditions, is necessary to form the requisite solid solution in matrices of these types.

Since the end of the last century, activated compounds have been studied in great detail, notably by Lenard and Klatt ([18]). These investigators prepared over eight hundred varieties of sulphide phosphor, whose properties they described in a series of papers published in 1904. These investigations were continued by Lenard and his collaborators and, more recently, by numerous other workers.

In the present section an attempt will be made to summarise briefly the very large amount of information which has accumulated regarding the properties of activated compounds.

The spectrum of the light emitted by these materials consists of one or more broad bands, whose relative intensity varies with the temperature and with the method of preparation of the compounds; at any one temperature one band tends to be predominant. The position of the band depends on the nature of both the activator and the matrix. Thus, for example, in zinc sulphide, copper or bismuth activators produce a green band, while manganese gives a yellow and silver a blue one. Typical spectra are illustrated in Fig. 2.

The effect of changing the wavelength of the exciting light is interesting. Provided that excitation is produced at all, the position and extent of the luminescence band remain practically the same, whatever the wavelength of the exciting light; only the total intensity of the luminescence varies. The intensity-wavelength distribution of the luminescence band for a typical case is shown in Fig. 3 by the curve marked E. At a given temperature the band E is emitted as *fluorescence* when excited by radiation of any wavelength falling in the range represented by the curve marked F. The height of this curve at any wavelength shows the relative total intensity of the emission band E excited by that wavelength. If, on the other hand, the exciting light is of any wavelength in the range defined by the curve marked P, the same band E is emitted as *phosphorescence*. Light whose wavelength lies in regions where the F and P curves overlap will naturally excite both fluorescence and phosphorescence. In general, the excitation curve P for phosphorescence has several distinct peaks, but that for fluorescence F is often broader and less defined. Each substance has its own characteristic set of these curves, which vary considerably in shape, height, and position in different cases; when there is more than one emission band a set of such curves belongs to each.

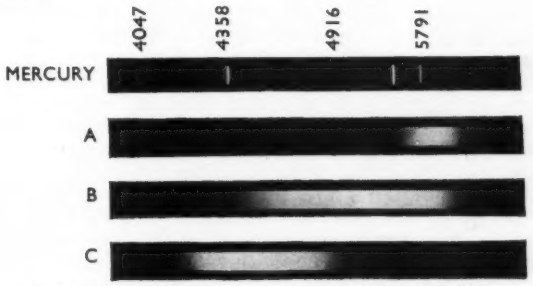

Fig. 2. Spectra of luminescent zinc sulphides with different activators.
A—manganese. B—copper. C—silver.

The effect of raising the temperature is to shorten the after-glow period, without reducing the total integrated energy emitted as phosphorescence. It has been found that, in general, the latter quantity is independent of the temperature, provided that the phosphor has been exposed to light sufficiently long for it to become "saturated." Warming the glowing phosphor will thus cause a brightening or acceleration of the light emission, since the same energy is then given out in a shorter time.

Irradiation of sulphide and selenide phosphors by longer wavelengths produces an extinction effect

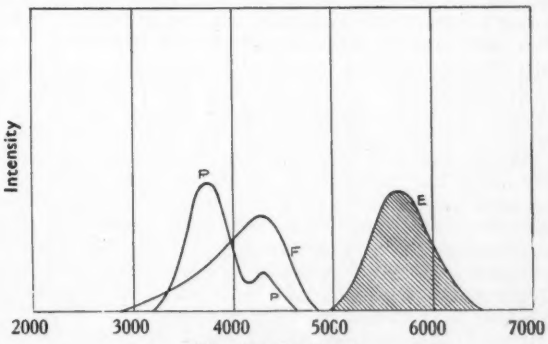

Fig. 3. Forms of excitation curve and emission band (diagrammatic only).
F, Excitation curve for fluorescence.
P, Excitation curve for phosphorescence.
E, Emission band.

whereby some of the stored energy in the phosphor is released as heat and the total light emitted is consequently reduced. This effect is often accompanied by an acceleration effect similar to that mentioned above as produced by warmth. The extinction effect of orange and red rays has been known for a long time, and was, in fact, first noticed by Goethe ([19]) when experimenting with the Bologna Stone. Later work has shown that the curve representing the efficiency of different wavelengths in producing extinction has peaks characteristic of the particular substance. A typical curve is shown in Fig. 4. This

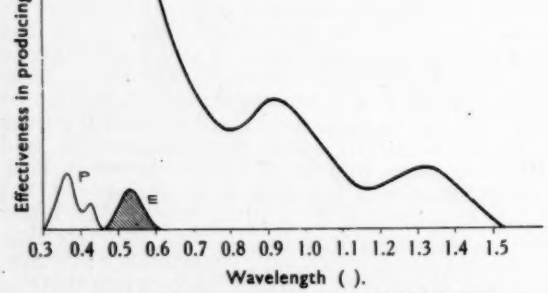

Fig. 4. Typical extinction curve I (sulphides). The emission band E and phosphoresence excitation curve P are also shown, but on a very much smaller scale.

shows the extinction curve I, together with the excitation curve P, and the emission band E, for a zinc sulphide phosphor activated by copper. It will be seen that for equal energy the shorter wavelengths are the more effective in producing extinction; infra-red is usually said to be the most effective because the incandescent sources generally used emit so much more energy in the infra-red than at shorter wavelengths.

When the materials are under continuous excitation by ultra-violet radiation the intensity falls off as the temperature is raised beyond a certain point. This temperature dependence of the intensity is of both theoretical and practical importance, and it has been studied by Curie ([20]) and more recently by Randall ([21]). A curve obtained by the latter for a particular zinc cadmium sulphide is shown in Fig. 5.

The intensity of the luminescence varies considerably with the percentage of activator in solid solution and passes through a maximum at a particular concentration, which depends upon both the activator and matrix. For example, in the silicates the optimum generally occurs between 0.5 per cent. and 0.1 per cent., while in zinc sulphide with copper as activator it is as low as 0.005 per cent.

In contradistinction to the class of metals which function as activators there are others, such as iron, which may act as " inhibitors." These, when present even in the most minute traces, can reduce the intensity of the luminescence very considerably. For this reason the very greatest precautions have to be taken to exclude these elements during the preparation of the luminescent compounds. In fact the modern practice, with sulphides for example, is to carry the purification to such a degree that no inhibitors are present even to the extent of one part in several million. In zinc and zinc-cadmium sulphides the presence of nickel in quantity as minute as one or two parts per million materially reduces the phosphorescence, although it has little influence on the fluorescence. On the other hand, quantities as large as one part in one hundred thousand seriously reduce the intensity of both effects. The use of nickel in minute proportions, to inhibit the after-glow, has been applied very successfully by Levy and West([22]) to luminescent sulphide screens used for X-ray work.

Other metallic " impurities " can act in the opposite manner when introduced into some materials. Thus calcium tungstate which, as already mentioned, appears to fluoresce without the presence of any known activator, can exhibit phosphorescence, with X-ray excitation, when an activator such as lead is

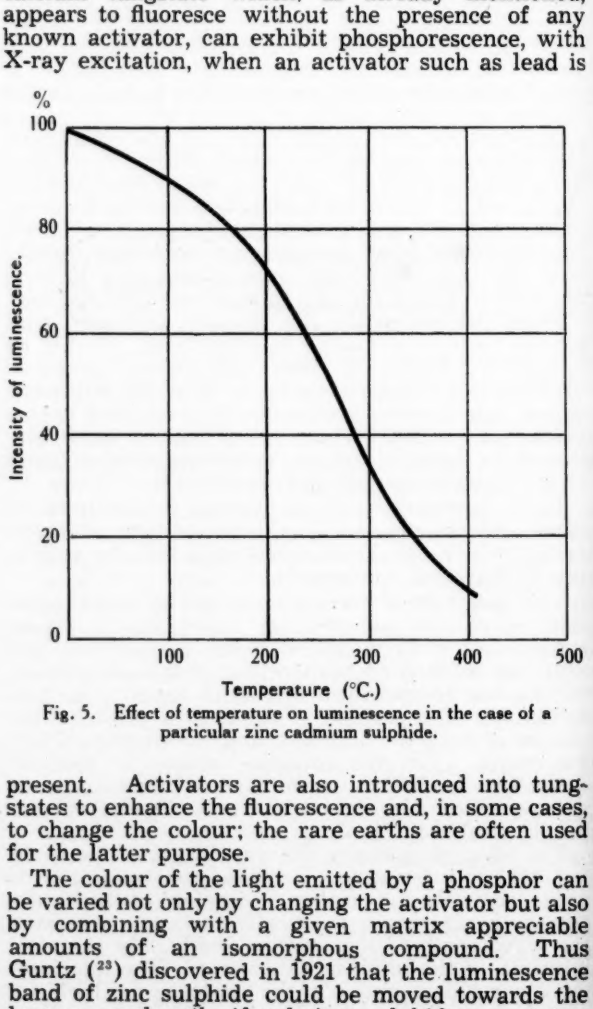

Fig. 5. Effect of temperature on luminescence in the case of a particular zinc cadmium sulphide.

present. Activators are also introduced into tungstates to enhance the fluorescence and, in some cases, to change the colour; the rare earths are often used for the latter purpose.

The colour of the light emitted by a phosphor can be varied not only by changing the activator but also by combining with a given matrix appreciable amounts of an isomorphous compound. Thus Guntz ([23]) discovered in 1921 that the luminescence band of zinc sulphide could be moved towards the longer wavelengths if cadmium sulphide were introduced into the matrix. In fact, by using a solid

solution of zinc and cadmium sulphides in suitable proportions, the band can be obtained in any desired position between the green and the red end of the spectrum. In the extreme case of cadmium sulphide without zinc the band moves so far out of the visible that the luminescence is not apparent.

Much the same thing occurs in the series of solid solutions of zinc and beryllium silicates. Thus the well-known green band of zinc orthosilicate moves towards the red end of the spectrum as the proportion of the isomorphous beryllium silicate is increased.

In the two examples just quoted, each family of solid solutions has the same crystal structure, but colour changes also occur when the same elements in the matrix combine in different proportions and crystallise in different forms. Thus zinc orthosilicate $2ZnO:SiO_2$ activated by manganese emits a green luminescence, but zinc meso-disilicate $ZnO:2SiO_2$ gives a yellow luminescence with the same activator. Spectra of these two compounds are shown in Fig. 6.

Before leaving this subject the possibility of preparing luminescent sulphides having no metallic

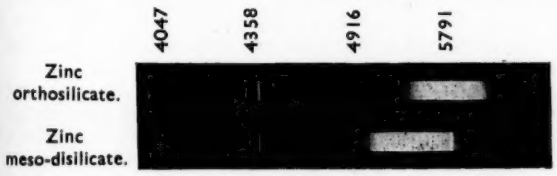

Fig. 6. Spectra of luminescent zinc silicates. (The lines are due to mercury.)

activator must be mentioned. The recent work of Schleede[24] shows that, in spite of the greatest precautions to exclude such activators, a form of zinc sulphide can still be prepared which shows fluorescence. The necessary condition would appear to be that the crystals must consist of twinned hexagonal and cubic structures. It is possible that the lattice distortions occasioned by the two different structures produce effects similar to those produced by the presence of activators.

Applications to Electric Dicharge Lamps.

Photo-luminescent materials have been applied in a great many ways, some of which have been described in a paper read before the society by F. E. Lamplough[25] and in the discussion which followed. Reference may also be made to a much earlier discussion in 1917[26] and to a recent paper by Randall[27]. Apart from the many scientific applications, a number of fluorescent dyes and other organic and inorganic materials are used, in connection with ultra-violet lamps, for producing spectacular effects; in these cases the substances are employed at some distance from the lamps, which themselves emit no appreciable amount of visible light. The application of the materials to light sources differs in that they are placed sufficiently near the source for their fluorescent light to become mixed with the primary light. When applied in this way, they provide a valuable means of utilising some of the otherwise wasted energy of the invisible radiation, and thus increasing the efficiency of the source; suitably chosen materials can, at the same time, improve the colour of the light by contributing radiation of wavelengths in which the simple source is deficient. Before proceeding to a detailed discussion of this application, a little must be said about the amount of invisible radiation available for conversion.

The energy supplied to a light source reappears in the following forms:—

(a) Ultra-violet radiation.
(b) Visible radiation.
(c) Near infra-red radiation.
(d) Thermal losses, which include the very long wavelength infra-red radiation.

Now, by Stokes's law, it follows that luminescent materials can be of no appreciable help in reducing (c) or (d); on the other hand, they provide an excellent means of transforming the wasted energy (a) into useful light. Thus, their useful application is restricted to those types of source which give a considerable amount of ultra-violet radiation; that is, practically speaking, to certain varieties of discharge lamp.

In the case of mercury discharge lamps in which the pressure is of the order of one atmosphere, the thermal losses (d) account for some 60 per cent. of the energy supplied. Roughly 12 per cent. is emitted as visible light, an equal quantity as near infra-red radiation and about 15 to 20 per cent. as ultra-violet, although much of the latter is absorbed by the glass envelopes. Thus, at this pressure, nearly twice as much energy is wasted in the ultra-violet as is emitted in the useful visible range. At lower pressures the proportion of ultra-violet to visible radiation increases, while at much higher pressures it becomes less. Clearly, then, there are considerable possibilities in the application of luminescent materials to mercury lamps. Valuable effects can also be obtained in the case of some types of neon discharge lamps, as will be described below.

With sodium lamps, on the other hand, practically nothing can be done in this way, since the amount of ultra-violet they emit is negligible. Roughly 14 per cent. of the energy supplied is radiated as visible light, while the remaining 86 per cent. appears as infra-red radiation and thermal losses.

It is possible to introduce a small amount of red radiation into the light, by means of reflectors coated with films containing rhodamine, but only at the expense of efficiency. This is because the red radiation is obtained by the conversion of some of the useful yellow sodium light, to which the eye has a fairly high sensitivity.

The proportion of the ultra-violet radiation available at the source which can be converted into useful light depends, in part, on the position of the luminescent substance in relation to the source, as well as

on the nature of the material used. There are three principal methods which may be employed:—

(I.) The materials may be placed on reflectors, which partially surround the lamp. In this case, only the near ultra-violet light from the lamp is available for transformation.

(II.) They may be placed on the inside of the outer glass bulb, which, in many types, surrounds the discharge tube proper.

(III.) They may be placed on the inner wall of the actual tube through which the discharge passes. In this case, all the ultra-violet radiation emitted by the discharge is available for conversion to longer wavelengths.

In general, organic materials are only applicable when the first method is used. In this case the problem is to find a combination of material and medium such that,

(a) the fluorescent colour is appropriate;

(b) the fluorescence efficiency is as high as possible for the given exciting light;

(c) the fading effect is reduced to a minimum.

As early as 1903, Burke([28]) suggested the use of liquid solutions of eosin or rhodamine to improve the colour of mercury lamps and later, in connection with the Cooper Hewitt lamp, celluloid films stained with rhodamine were employed, to make up for the deficiency of red in the low-pressure mercury spectrum. With the advent of the new high-pressure varieties of discharge lamp the interest in this early method of colour correction revived, and further investigations on suitable organic materials were carried out, notably by Fonda ([29]). With the new type of lamp, liquid solutions were naturally out of the question, for practical reasons, so that solid solutions had to be used, but rhodamine still proved to be the most suitable of the numerous dye substances investigated. With regard to the medium, Fonda measured the energy ratio of fluorescent to exciting light for rhodamine contained in films of various materials such as cellulose acetate, nitrocellulose, gelatin and glyptal resin. The films were prepared by adding the dye to liquid solutions of the media and evaporating the solvent. The most satisfactory proved to be cellulose acetate, for which, using a mercury lamp and the optimum concentration of the dye, the ratio was found to be 44 per cent. Not only did cellulose acetate give the greatest fluorescence, but it was also the medium in which the fading was least rapid. On the other hand, Randall and McKeag([30]) have found that media composed of certain synthetic resins are very effective in reducing the rate of fading, provided that the dye is dissolved directly in the molten resin, in the absence of other solvent. Reflectors may be coated by applying the material in the molten state to the heated surface or by allowing it to melt in contact with the surface at about 200° C. The rate of fading is also dependent on the exact chemical constitution of the dye. This question has also been studied by Fonda, who has prepared special derivatives of rhodamine, which fade much less rapidly than the ordinary variety; the most effective of these was a potassium salt.

In view of the difficulty of the fading experienced with organic fluorescent materials, when used with high-pressure mercury lamps, the author([31]) in 1932 proposed the use of zinc cadmium sulphide phosphors. Investigation showed that when these compounds were applied, in powder form, to the reflector, they provided sufficient red light for many purposes and would withstand practically indefinitely the stringent conditions imposed by the close proximity of the high-pressure mercury lamp. Further work then showed that the powders could with advantage be placed on transparent plates or cylinders, surrounding the lamp. In actual practice the best position for the powders was found to be the inside of the outer jacket of the lamp, that is method II. By placing them in this position, the accumulation of dirt on the materials during use, which would lower their efficiency, was completely avoided.

The red luminescent powders tend to absorb a certain amount of blue light, and, to counteract this, a little cadmium may be introduced into the discharge. The cadmium, which emits far more blue light than red, makes up for that absorbed in the phosphorescent layer and thus improves the colour, although, as always, the cadmium produces a drop in efficiency. Alternatively, blue luminescent powders may be used in addition to the red.

Lamps of the above type appeared on the market towards the end of last year; they are rated at 400 watts and give an efficiency of 37 to 38 L/W with 5 to 6 per cent. red. An example is shown in Fig. 7. Fairly large outer bulbs are used in order to keep the temperature low, since, as mentioned in a previous section, the luminescence of the sulphide phosphor diminishes at higher temperatures.

In the lamps just described the discharge tube proper is made of a special hard glass, but, although

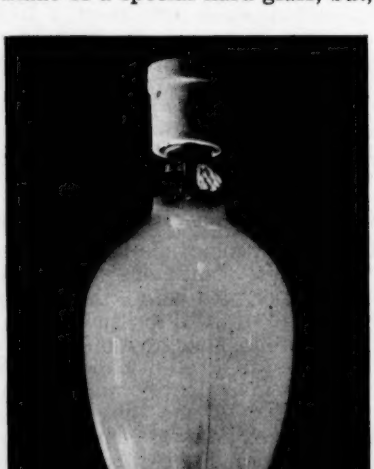

Fig. 7. 400-watt Luminescent Lamp.

precautions are taken in the manufacture to keep the iron content as low as possible, the shorter ultra violet wavelengths are absorbed. For this reason, only those luminescent materials which are excited by the longer wavelengths are employed.

It remains to describe the application of luminescent solids to low-pressure mercury and neon discharge tubes. In this field method III, the most effective of all, can be employed, and it has enabled many striking advances to be made.

The development may be traced back to the middle of the last century when Becquerel ([32]) exposed layers of the then known luminescent compounds to electric discharges, in tubes containing rarefied air; he also, on occasion, stuck the materials to part of the inside surface of the tubes. Later, screens coated with willemite were employed in connection with cathode ray experiments, but no application of the compounds to practical light sources was made. Indeed, although the modern types of high-voltage mercury and neon discharge tube were introduced by Claude in 1913, luminescent materials, other than uranium glass, were not applied to them until many years later. One difficulty was the production of sufficiently thin and uniform layers of the compounds on the inside of the tubes, and another was the tendency of the binders to decompose and to evolve gas, with disastrous results. It is thus not surprising that Risler ([33]), who, in 1923, proposed to apply the powders either inside or outside the tubes, preferred in practice to employ them on the outside. He used sulphide phosphors, which could be excited by mercury radiation transmitted through the glass, but although new tints could be obtained by these means, the method was little used, and it was not until 1932 that a more practical process was evolved ([34]). This depended on the production of an extremely thin and even layer of a suitable binder by driving a bung through the tube, by means of compressed air, for example. The luminescent compound, in powder form, was then run through the tube and was retained as a thin and very uniform coating. Sulphide phosphors were used for the first tubes to be marketed and enabled a variety of new colours to be obtained. Considerable attention was then given to the development of special silicate and tungstate compounds for this purpose, and these soon replaced the sulphides almost entirely. This was because the newer compounds were excited by a greater range of the ultra-violet and led to much greater luminous efficiency.

In 1935 H. G. Jenkins ([35]) discovered that the more efficient zinc orthosilicate and calcium tungstate compounds could be excited strongly by the pure neon discharge. He found, moreover, that the brilliant green fluorescent light and the orange-red radiation from the neon combined together to give a bright yellow subjective colour. Similarly, the blue from calcium tungstate combined with the neon light gave an attractive pink. Previous to this, a good yellow could only be obtained by the use of helium gas in a yellow glass tube, which method had many disadvantages; the efficiency was not very good, and special electrodes had to be used. Although neon emits very little ultra-violet light in the range of wavelengths transmitted by glass, or even by quartz, it, nevertheless, radiates strongly in the far ultra-violet region. In fact, the neon spectrum contains powerful series of lines commencing at 735 A.U. and 744 A.U. respectively, and the excitation of the powders is to a large extent due to radiation of these wavelengths.

The discovery mentioned was of importance, not only because of the new colours, but also because the brightness of the neon excited tubes was found to remain almost the same after three or four thousand hours' burning as it was initially. This practically perfect lumen maintenance cannot be achieved when mercury is used for excitation; there is then always a certain falling off of brightness during life, due, at least in part, to the formation of an absorbing film over the surface of the powder.

Instead of coating the inside of the tube with luminous compounds, glasses may be used which are themselves fluorescent. The earliest example was uranium glass, which is still employed extensively for sign tubes at the present time. Recently a number of additional varieties have been developed; these depend for their effect on the rigorous exclusion of iron and the introduction of various substances, which then produce fluorescence ([36]). The tubes are sometimes made in layers, one of which may contain colouring matter; this, by absorbing certain wavelengths, can produce further modifications of the colour. A disadvantage of incorporating materials producing fluorescence in the glass itself is that it is not possible in this way to convert so large a range of wavelengths into visible light as can be done by the powder coating method. For one thing, the glass itself absorbs ultra-violet of some wavelengths, and for this reason fluorescent glass tubes are not excited by the pure neon discharge.

From the point of view of advertising signs and decorative work, the application of luminescent materials has greatly increased the range of colours available, and has also enabled brighter tubes to be obtained, without increasing the power consumed. In this field the requirements are that the tubes themselves shall give attractive new colours or tints at high efficiency. When, on the other hand, the tubes are to be used for interior illumination, the light must satisfy three additional conditions, namely, that it must be aesthetically pleasing, that it must be becoming to the human complexion, and, lastly, that it must give reasonably good colour rendering of objects.

It may be noted that these requirements by no means necessitate that the colour should be like daylight on the one hand or like light from incandescent filament lamps on the other.

Various degrees of "warmth" or "coldness" are often desirable, according to circumstances, and these can be obtained by combining different types of tube. For example, an arrangement consisting of a mercury excited zinc orthosilicate tube with a neon tube on each side is often used. Alternatively, three different tubes comprising high efficiency neon, zinc orthosilicate excited by mercury, and calcium tungstate excited by mercury give good results. If desired, the tint of the combined light can be varied

continuously by changing the current passing through the different tubes. Tube combinations consisting of neon excited calcium tungstate with mercury excited zinc meso-disilicate may also be mentioned.

Members of the recently developed zinc-beryllium series of luminescent compounds, when in mercury excited tubes, produce colours which may range from yellow-green to orange and from creamy white to pink ([37]). Certain of these powders, sometimes blended with other types, enable a variety of tints of nearly white light to be produced. Tubes containing these compounds appear to be particularly suitable for interior illumination, both on account of their relatively high efficiency and of the pleasing character of the light they produce. Moreover, one particular variety of zinc-beryllium silicate gives an excellent white of the type required in advertising sign and decorative work.

The brightness and colour of the tubes employed for interior lighting is generally such that they can be used without the tinted diffusing fittings that so often reduce the efficiency of incandescent lamps. Installations of the tubing also produce very good light distribution because of the extended nature of the sources.

The efficiencies and colours of high-voltage tubes containing various luminescent compounds are given in Table I.

TABLE I.

Efficiency of 50-watt high-voltage tubes. Length 2.7 metres, diameter 15-20 mm., current 35-60 mA.

Gas or vapour filling	Luminous Powder used	Resultant colour	Luminous efficiency of tube in lumens per watt Average values
Mercury	None	Pale blue	5
	Zinc orthosilicate	Bright green	50-60
	Zinc meso-disilicate	Yellowish white	25
	Zinc - beryllium silicates (various)	Pink to cream white	30-40
	Calcium tungstate	Deep blue	15
	Magnesium tungstate	Light blue	30
High efficiency neon	None	Orange red	15
	Zinc ortho-silicate	Yellow	22
	Calcium tungstate	Pink	15

Development is proceeding on the lines of increasing the intrinsic efficiencies of the powders, discovering new ones and improving the coating technique. With some powders, much higher efficiencies than those quoted have been obtained in the laboratory; in fact, in the case of zinc orthosilicate, an efficiency of nearly 100 lumens per watt has been reached. This silicate material is, of course, the most favourable from the point of view of luminous efficiency, since its emission band is in the green part of the spectrum, to which the response of the eye is the greatest. Conversion of the same amount of ultra-violet energy into light of other colours, such as blue or red, necessarily produces less lumens, and, therefore, leads to a smaller gain in efficiency. It follows that, if materials are chosen to give a more or less white light, such a high efficiency is not to be expected. Tubes are, however, under development, which give excellent colour at efficiencies between 30 and 40 L/W.

The latest varieties of luminescent powders are also being applied to experimental low-voltage tubes; these are somewhat similar to the low-pressure hot cathode floodlighting lamps already on the market. Many new problems arise in connection with these tubes, but, from the point of view of the application of luminescent materials, they can be considered as shorter versions of the high-tension types; much the same colours and efficiences can, therefore, be obtained.

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DISCUSSION

Mr. F. E. LAMPLOUGH, who opened the discussion, said that he personally greatly appreciated the many experiments which the author had shown, and especially the projection of a bright spectrum, which was a difficult thing to do. The paper and experiments were a striking example of the extraordinary manner in which modern science was becoming more and more complicated and of the way in which a phenomenon, which at first appeared simple, had developed into a special science involving a wealth of experiment and complex theory.

As regards the paper itself he had no criticism to offer. Some of the phenomena connected with selective fluorescence had a special interest to him, and he would be glad to have any information that was available respecting certain tungstates which the author had demonstrated during the lecture, and which were inactive to a band in the near ultra-violet, including the powerful mercury vapour line at 3,650 A.U., but showed good luminescence under radiation of longer and shorter wave-lengths.

Mr. L. J. DAVIES said that although the author had mentioned the phosphorescence of solid inorganic materials, he had not mentioned—although no doubt he knew about it—that "quartz" itself in the fused transparent state exhibited phosphorescence. He did not know whether this material showed this effect when it was completely pure; but rather believed that some connection could be traced between the phosphorescence and the gaseous impurities adsorbed in the quartz, although he was not quite sure about that.

Mention had been made of the application of fluorescent powders for the correction of colour to discharge lamps, and the author had shown on the screen how the size of the outer envelope was increased. This reduced the intrinsic brilliancy of the lamp to some extent, but he would be interested to know how the lamp was handled and regarded by the lighting engineer, particularly if its use was attempted in directional fittings.

He was also very interested in the long tubular light sources of high efficiency which had been described because they differed from the high pressure mercury vapour lamp, amongst other things, in that they could be switched on and off with thermal delay period. This meant there would be new spheres of application for this type of lamp.

Reference had also been made to general applications of fluorescent materials. An important one is that in which a dye is used to mark laundry. Although, perhaps, this hardly came within the scope of the paper, it is an extremely useful application in that it enables the speeding up of the sorting of articles at laundries by simply passing them under an ultra-violet lamp.

Mr. J. T. ANDERSON said that in his historical review of the subject the author had rather done a disservice to Zucchi who, as early as 1652, discovered that the *phosphorescent* colour was independent of the colour of the light previously shone on the Bologna stone. Nevertheless the fact that it took 250 years for the same effects to be noticed with regard to *fluorescent* light was remarkable, and in a way reflected credit upon the remarkable achievements of Mr. Ryde and other workers in this field who had accomplished so much in the past ten years. One rather important point had been omitted from the paper in that there was no mention of a rather unique body of phosphors, namely inorganic bodies activated by organic substances, e.g., the Boric Acid Phosphors, to which increasing attention was being given, particularly in the U.S.S.R. With regard to the tungstates being only active when irradiated by short ultra-violet it might be worth mentioning that there was one tungstate, at least, which when suitably activated was almost equally bright with the long wave ultra-violet radiation as with the short.

Mr. G. H. WILSON said that the paper gave proof of the variety of knowledge that the illuminating engineers should possess at the present time. It was evident from what the author had shown that for this sort of experimental work, at all events, a man needed to be a physicist, a chemist, and an electrician all rolled into one. He had been interested in the author's photometric data for the firefly. Whilst the firefly, in comparison with modern light sources, was not very bright, he had found that it was about sixty times as bright as a well-lighted road surface! Therefore, in comparison with some of our modern street lighting, the firefly did not do so badly. There was little doubt that these new light sources would provide new tasks for the illuminating engineers who would be concerned with fittings design in the near future. The point had been made by the author, however, that with many of the long luminous tubes

which he had shown, decorative lighting could be obtained without the use of any fittings at all.

He would like to ask whether the author thought that with these new sources of light, which had high efficiency and yet low brightness, it might be possible in the fairly near future to have values of illumination of the same order as those experienced in daylight, i.e., that one might produce illuminations of hundreds or thousands of foot-candles without danger of glare.

Mr. J. S. Dow remarked that whilst everybody was impressed by the possibilities of fluorescence, they were conscious that knowledge of phosphorescence lagged behind. For instance, we were as yet a long way from the ideal of a wallpaper which would absorb energy by day and emit at night enough light for purposes of illumination. It had always seemed to him that we know little about the conditions which determined the intensity and duration of phosphorescence. He wondered whether there was any accurate knowledge of what determined the storage capacity of a substance, how far the intensity of the excitation could be made greater and greater, if more and more energy was pumped into it, and whether the duration of the luminous effect could be made long enough to be of practical value—i.e., whether, if the material were subjected to a really strong dose of energy, the effect could be made to last for a long time.

It was evidently possible to get a large increase in candle-power with a lamp which was normally almost non-luminous if a suitable coating were applied. But when such a coating was applied to the ordinary discharge lamps, resulting in improved colour of the light, would there be any material improvement in efficiency?—because the luminescent coating, whilst giving the benefit of increased light owing to excitation by the ultra-violet rays might also absorb so much visible light that the net gain might be small.

Another matter was the difficulty, as it seemed to him of determining accurately the lumens per watt of such light sources as had been shown. One had to deal not only with a peculiar colour, but also a source of very large dimensions.

Finally, Mr. Dow asked whether the use of fluorescent coating tended to diminish cyclical variations in light from a discharge lamp? If there was a certain lag in the effect of the fluorescing light, then, presumably, the variations due to the a.c. supply would not be so great as with the ordinary discharge lamp. This might be a distinct advantage in certain forms of industry where stroboscopic effects were liable to prove troublesome.

The PRESIDENT said he was rather impressed by the problems involved in applying the fluorescent type of lamp to directional lighting equipment. The author had stated that at the present time it was necessary to limit the temperature to less than 170° C., in order not to kill the fluorescent material. Was there any expectation of getting a fluorescent material which would stand up to a higher temperature. If such a material could be found he hoped it would be possible to design a fluorescent type of lamp with very much smaller dimensions than the present ones, thus diminishing the difficulties he had mentioned. If the author could hold out any hopes along these lines he was sure many designers of lighting fittings would be grateful.

Mr. S. J. PATMORE, commenting on the fact that these fluorescent or luminescent materials were affected by the ultra-violet light of the atmosphere and gradually became ineffective, asked the author whether there were any means of preserving the effectiveness of them when they were used outside in the atmosphere.

Mr. SCOTT remarked that the effect of temperature on fluorescent materials had been mentioned on several occasions during the discussion. Mr. Ryde had pointed out how in the 400-watt fluorescent jacket lamp, the jacket size is such as to keep the powder temperature suitably low. This large jacket gives us a lamp very suitable for use in diffusing type fittings for industrial and area lighting, but the lamp is not at all ideal for directive fittings, such as are now in use for highway lighting. There appears at the moment only one way of reducing the lamp size with the available fluorescent materials—namely, to bring the powder close to the high intensity source, and at the same time artificially cool it. One such experimental lamp, using a 600-watt water-cooled quartz mercury lamp source, has given good colour correction with a water-cooled fluorescent screen fitting very closely around the lamp.

Turning to the low-pressure mercury vapour fluorescent tube it is of interest to note that this is singularly comparable with the sodium lamp, which it otherwise resembles so little, in that both lamps use the resonance radiation of the metal filling. This entails that, as in the case of the sodium lamp, care must be taken that the lamp is operated in an optimum temperature range for efficient light production. Fortunately, this temperature, which is of the order of 40° C. for the tubular fluorescent lamp, is very suitable for efficient fluorescent powder excitation.

Mr. R. O. SUTHERLAND said he was specially interested in the application of what the author had described and demonstrated, so far as decorative lighting was concerned, and he had already had questions asked him as to the life of these developments. As regards the lamps themselves, that was a matter of calculation, and he believed it had been investigated, but in the matter of using these powders behind glass for murals there were no data on the subject. The same thing applied to dyes in curtain materials, etc., where marvellous effects could be obtained but the dyes did die!

Speaking of the ultra-violet lamp he said he had noticed a certain amount of visible light having a kind of bluish purple colour, and if there were such light then an attempt ought to be made to use it in some way attractively. It would be interesting to know whether that sort of visible light would always be a factor. It was the fact that when glass was put before the lamp, marvellous colour effects were

obtained from the actual visible light, but, of course, the invisible light and its characteristics constituted the major importance.

Mr. A. W. BEUTTELL remarked that many people were interested in the permissible limits of surface brightness which might range from five candles per square foot possibly to fifteen candles per square inch. It would be interesting to know where some of these new lamps stood with regard to that question of the limits of surface brightness.

Mr. J. W. RYDE, replying to the discussion, said that as regards tungstates, which had been mentioned by Mr. Lamplough and Mr. Anderson, the excitation ranges varied with different compounds. The particular powder demonstrated was a magnesium tungstate which had been chosen to contrast with the other materials shown. He would have liked to have said something of Zucchi's early discovery, but, in a short historical survey, it was difficult to refer to all the important steps without being tedious. If the work of Goethe had been somewhat emphasised it was because so little was generally said of his experiments in the usual accounts.

The phosphorescence of quartz had been referred to by Mr. Davies, and he believed he was right in saying that, many years ago, Mr. Davies had published a note in "Nature" in connection with this. (In this note*, it was stated that after the passage of a discharge through a fused quartz tube containing oxygen or hydrogen, the quartz phosphoresced). He, the present author, was rather doubtful that the luminescence depended on the presence of occluded gases, but thought that other impurities probably had an effect. Mr. Davies also referred to the 400 watt fluorescent lamp that had been shown on the screen. That lamp was primarily developed for industrial work. Although the light from the plain high pressure mercury lamp was very good for showing all colours except red, difficulties were sometimes experienced in distinguishing reds from browns. By the introduction of red from the luminescent powder it was possible clearly to distinguish these colours. That was one of its uses, but it had others. In fact, it was being used in street lighting and in directional fittings. In this latter connection, was the point raised by Mr. Davies as to whether it was possible to control the fluorescent light as well as the primary light from the centre column by directional fittings? Measurements had shown that in a suitably designed asymmetric street lighting unit, for example, adequate control of both could be obtained.

Mention had been made of luminescent squids, but he thought that one of the most surprising and extraordinary cases was the fish *Photobleparon*, in which the light organ consisted of a mass of bacteria which lived in the fish perfectly happily and provided light. The fish had a sort of eye-lid which it could open and close and so was able to flash its light at will. The well-known boric acid phosphors had not been dealt with in the paper owing to lack of time; they were certainly very interesting, but he thought that their luminescence was not as great as that of sulphides.

As to Mr. Dow's question concerning the possibility of phosphorescence being used for general illumination, it would seem very unlikely that enough energy could be stored to ensure both high brightness and a sufficiently slow rate of decay. On the other hand, for special purposes, large areas coated with the compounds were useful. For instance, he believed that they were already being used in some of the air-raid shelters so that, if the lights were suddenly cut off, the people in the shelter would not be left in complete darkness and would have enough light to see their way about and prevent themselves from bumping into things. To that extent Mr. Dow's dream had been realised already.

As regards Mr. Dow's point in connection with the absorption of visible light by the powders, it was true that some powders did absorb to a certain extent, but this was generally counterbalanced by their fluorescence. In the quartz high-pressure mercury lamps it was possible to obtain a 20 or 30 per cent. gain if one did not mind about the colour, but if the best colour were required, then the efficiency was much the same with or without the powder. As to the photometry of large and coloured light sources, a great deal of work had been done on the subject during the last few years. In general, quite high accuracy was now obtainable, but the tolerances which the photometric people placed on their readings were certainly larger than in the case of tungsten lamps. Then there was the question of flicker, also mentioned by Mr. Dow; in some of the lamps it was possible materially to reduce the flicker by means of powders having an after-glow.

The point had been raised by the president that if powders could be obtained which did not drop in efficiency with temperature, then it would be possible to make the fluorescent lamps much smaller. There were some compounds known which were much less sensitive to temperature than others and one or two even improved with temperature up to a point. But as the choice of powers used depended on so many considerations there seemed little likelihood, at present, that the bulb size of the lamps could be reduced unless the powder were artificially cooled, as mentioned by Mr. Scott.

The question of the deterioration of luminescent compounds had been raised by Mr. Patmore and Mr. Sutherland. In the case of inorganic compounds, such as zinc sulphides, the deterioration was due to a chemical change. When the compound was exposed to a strong light in the presence of even a trace of moisture, the zinc was reduced and the powder blackened in consequence. If, however, the powder were incorporated in a suitable medium which adequately protected it from the atmosphere. little or no deterioration took place. In the case of fluorescent organic dyes, the rate of fading de-

*D. L. Chapman and L. J. Davies, Nature, 113, p. 309 (1924).

pended greatly on the medium in which the dye was dispersed. The amount of moisture present also affected the rate of fading of dyed materials and this made it difficult to give definite data for the rate of fading, except in reference to rigidly controlled conditions.

As regards the surface brightness of the various lamps, which had been mentioned by Mr. Beuttell, the various low-pressure tubes demonstrated varied from about 1 to 3 candles per square inch; they were thus quite suitable for interior illumination without the use of diffusing fittings.

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